

**MODIFIED ACRYLIC BASED COMPOSITIONS OF ENHANCED OPTICS
AND LOW TEMPERATURE IMPACT STRENGTH**

BACKGROUND OF THE INVENTION

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Field of the Invention

The present invention relates to the preparation and use of acrylic based compounds for injection molding applications and the preparation of polymer films and sheets having improved optical and thermal properties, that are particularly suited for a variety of industrial applications.

Description of the Related Art

15 Polymethylmethacrylate (PMMA) resins are well known for their exceptional clarity and good weatherability and find applications such as automotive, glazing, packaging, etc. The impact properties of these polymers have been improved by blending butyl acrylate impact modifiers polymerized by free radical emulsion polymerization. However, impact modified PMMA resins generally possess relatively poor impact properties at sub-zero temperatures, thereby limiting their use in this temperature range.

Acrylic based multipolymer compounds, like Acrylite XT® polymer & CYROLITE® are impact modified with polybutadiene modifiers and retain high level of impact strength at substantially lower temperatures than the corresponding PMMA grades, *i.e.* -80°F. However, the optical properties of state of the art polybutadiene modified resins is deficient relative to the optics of PMMA resins.

Accordingly, a need exists for an improved class of resin compounds and compositions that offer improved thermal and optical properties and performance in a broad range of environmental conditions.

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SUMMARY OF THE INVENTION

The present invention provides acrylic based multipolymer compositions having enhanced optical properties, comparable to impact modified PMMA resins, good sub-zero temperature impact strength similar to that of the Acrylic Based Multipolymer

10 Compounds, like XT® polymer & CYROLITE®, and improved weatherability. These compositions comprise a blend of:

15 A) an acrylic based multipolymer, comprising in weight %: 8-12% acrylonitrile, 3-8% butyl acrylate, 3-5% ethyl acrylate, 3-8% methyl acrylate, 65-80% methyl methacrylate, and 15-30% styrene.

B) a methylmethacrylate-butadiene-styrene (MBS) copolymer modifier polymerized by a free radical process.

20 C) commercially available UV stabilizers, including benzotriazole derivatives, triazine derivatives, and hindered amine light stabilizers, as single components or combinations thereof.

25 D) a combination of commercially available antioxidants, dyes and plasticizing flow enhancers.

In a particular embodiment, the composition comprises, in weight percent, from 55 to 85% of component A, from 15 to 45% of component B, up to about 0.5% of component C, and up to 5.0% of component D.

More particularly, the invention extends to such compositions displaying the combination of improved optical properties and sub-zero temperature stability, that are prepared by a method that includes the blending of components to achieve a Refractive Index (RI) that tolerates a maximum mismatch between components of 0.001 refractive index units.

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In a further aspect, the invention relates to an acrylic based multipolymer composition wherein the auxiliary polymer additives have composition within the following range, in % by weight:

10	Formula A, low refractive index:	methyl methacrylate	92-98%
		methyl acrylate	2-8%
	Formula B, high refractive index	methyl methacrylate	30-50%
		styrene	45-70%
		acrylonitrile	8-12%
		ethyl acrylate	3-8%

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The inventive compositions may include up to 5% of lubricants, processing aids, and plasticisers. Further the compositions may contain up to 0.5% of UV stabilizers, and such stabilizers may in turn, comprise benzotriazole derivatives, including benzotriazole derivatives selected from the group consisting of 2-(2'-hydroxy-5'-methylphenyl) benzotriazole, triazine derivatives, *e.g.* 2-(4,6-diphenyl-1,3,5-triazine-2-yl)-5-hexyloxy)phenol, or hindered amine light stabilizers, and combinations thereof.

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As stated above and herein, the compositions of of the invention exhibit the retention of room temperature impact strength tdo a commercially significant level at sub-zero temperatures, as low as -80°F. Accordingly, numerous formed products may be prepared that take advantage of the mechanical and optical properties exhibited by the present compositions.

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Other objects and advantages will become apparent to those skilled in the art from a

consideration of the detailed description that proceeds with reference to the following illustrative drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

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Figures 1 and 2 and TEM micrographs of the impact modified acrylic based resin of Example 1.

DETAILED DESCRIPTION OF THE INVENTION

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The improved impact strength of the products is due to microphase separation of the polymer blend, the particle size of the rubber phase being a critical factor in control of the underlying fracture mechanics. A suitable particle size range is from at least about 50 nanometers (nm) and can be on the order of 100 nm or more.

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The small size modifier particles in the hard phase as seen in TEM micrographs (Figures 1 and 2), the good mechanical properties like impact strength, ductility (*i.e.* elongation at break), as well as other key properties which would be adversely affected in an incompatible alloy/blend, all suggest a favorable compatibility of the MBS modifier with the multipolymer matrix. The reason why clarity is maintained is because of refractive index matching between the modifier and the hard phase. The common methods of monomer blend composition control do not provide access to the range of 0.001 refractive index units, critical for the target optical properties. In the present invention, this high level of accuracy is achieved by a process of controlled feeding of auxiliary polymer additives that have different refractive index from and are miscible with the multipolymer hard phase.

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It is possible to modify the Refractive Index (RI) of transparent acrylic plastics by means of mechanical blends of polymers of varying RI's. This can be used for RI adjustment of

the acrylic resin to the target RI of the impact modifier. The method is useful in the following cases:

- Compensation for process variation of acrylic resin RI
- Compensation for impact modifier RI
- 5 Compensation for impact modifier RI changes due to extruder condition changes

Incompatibility is a common phenomenon in polymers and results in microphase separated opaque polymer blends. Miscibility of the polymer components of the matrix material is critical for the optical clarity in the current applications. For this reason, the auxiliary resins for RI adjustment are carefully designed to be completely miscible with the acrylic resin. They are acrylonitrile/styrene/acrylic copolymers of varied composition tuned to the desired refractive indices. The blends are prepared by feeding an extruder with precision loss-in-weight feeders which control the ratio of the base polymer and the RI modifying polymer. The overall RI can be approximated to the sum of RI

10 contributions proportional to the volume fractions of the individual polymer components. Experimental work has shown that with proper comonomer selection, the RI of the basic acrylic resin can be adjusted within a relatively broad range, *i.e.*, 1.49 to 1.60. Particular examples of procedures for polymer preparation and processing that seeks to optimize RI match of the components, are set forth below.

20 In a first example, the base acrylic polymer is intentionally modified to optimize the RI match to the impact modifier. A 6" diameter Welding Engineers, non-intermeshing, counter rotating, 36/L/D devolatilizing extruder was fed with an acrylic copolymer and impact modifier. The polymer was fed with a LUWA Vacurex 110/110 metering pump

25 and the modifier with an Acrison 403 Loss-In-Weight (LIW) feeder with micro-date control. A portable Acrison 403 LIW was used to feed acrylic copolymers of high and low RI's optimizing the RI match.

A second example of this technique was carried out using a 50/1 L/D, 4-1/2" two stage,

single double wave screw compounder. Three Technetic LIW feeders were used, one for the impact modifier, the second for the base acrylic copolymer and the third a tumble blend of the base polymer, additives and the RI modifying acrylic copolymer. This again, allowed an optimization of the RI match between the various phases.

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Novel Features: A combination of optical clarity surpassing the optical properties of conventional polybutadiene impact modified acrylic compounds and retained impact strength at sub-zero temperatures, with particular strength measured at about 1 to 2 foot-pounds per inch.

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Utility of Invention: Improved appearance and color due to enhanced optical clarity. Applications in wider temperature range, as low as -80°F.

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The present invention will be better understood from a consideration of the following illustrative examples presenting formulations and their properties and characteristics, it being understood that the following are illustrative and not restrictive, and that all percentages are expressed in weight unless otherwise specified.

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EXAMPLES

The following compositions were prepared for use in the preparation of formed products that could be tested for optical and impact properties.

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<u>Formulation 1:</u>	Terpolymer of methyl methacrylate, styrene and	
	Ethyl acrylate	64.25%
	Kane-Ace B-564, supplied by Kaneka Texas Corp.	35%
	Plasticizing agent, stearyl alcohol	0.4%
	Antioxidant, Irgafos 168 powder	0.2%

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UV stabilizing agent, Tinuvin P 0.15%

Colorants for color matching, proprietary composition

Formulation 2: Commercially available impact modified acrylic molding and extrusion compounds, comprising polymethylmethacrylate, methyl acrylate, and butyl acrylate, with a BA modifier comprising methyl methacrylate, butyl acrylate and styrene, with a representative composition commercially available as ACRYLITE PLUS® ZK-6 by CYRO Inds.

Formulation 3: Commercially available impact modified acrylic molding and extrusion compounds, comprising polymethylmethacrylate, ethyl acrylate and styrene, and a MBS modifier comprising methyl acrylate, styrene and butadiene, with a representative composition commercially available as CYROLITE G-20 HIFLO® by CYRO Inds.

The above formulations were used to prepare formed samples for testing as to optical and mechanical properties. The tests were conducted in accordance with known industry standards (ASTM), and the results are set forth in Table I, below.

TABLE I

	<u>ASTM Test</u>	<u>#1</u>	<u>#2</u>	<u>#3</u>
<u>Optical Properties</u>				
- Transmittance (%)	D1003	91	91.5	89
- Haze (%)	D1003	1.1	1.0	3.5
- Yellowness Index	D1003	-2.0	0.4	-0.5
<u>Mechanical Properties</u>				
- Tensile Strength, psi	D 638	5500	6800	7,000
- Tensile Modulus, psi	D 638	240000	260000	370000
- Tensile Elongation				

	@ Yield (%)	D 638	4.0	5.0	3.8
	@ Break (%)	D 638	35	50	9.5
	- Notched Izod, ft-lb/in				
	1/4"bar @ 23°C	D 256	1.5	1.0	1.9
5	1/4"bar @ 0°C	D 256	1.2	0.6	1.1
	1/4"bar @ -32°C	D 256	1.0	-	-
	-Rockwell Hardness (L)	D 785	45	35	27

Rheological Properties

10	- Melt Flow Index, g/10 min				
	@230°C, 5.0 kg	D1238	9	-	12
	@230°C, 3.8 kg	D1238	-	1.6	-

15 B. Examples of applications

Acrylic based multipolymer molding and extrusion compositions may be prepared with particular ingredients and in the range of percentages as stated in claims (7), (8), (9), (10), (11), and (12) which are used in applications requiring toughness and transparency at low

20 temperatures, including transparent mechanical tool handles; transparent refrigerator bins, shelves, or doors; medical filter housings; IV connectors; medical storage or treatment trays; dental treatment device handles; and commercial display shelves and components.

25 C. Chemical Compositions

Component A: acrylic based multipolymer as described above.

Component B: a high rubber graft copolymer, wherein said graft copolymer may

30 comprise:

- from 50 to 95 percent by weight of a conjugated diene polymeric substrate having a glass transition temperature below -60° C. An exemplary resin is an emulsion polymer of 1,3-butadiene.

- from 5 to 50 percent by weight of a rigid superstrate copolymer having a glass

transition temperature greater than or equal to 50°C and consisting essentially of repeating units of a vinyl aromatic monomer and one or more (C₁ - C₁₂) alkyl (meth)acrylate monomers, wherein at least a portion of the rigid superstrate is grafted onto the diene polymeric substrate. An exemplary grafted shell is the copolymer of
5 methyl methacrylate and styrene with a low content of a cross-linking agent.

Components C&D: UV stabilizers, antioxidants, dyes etc. These are conventional additives used to enhance processability and certain performance parameters.

10 This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present disclosure is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended Claims, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

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